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THE DEVELOPMENT OF HEAT-RESISTANT PAINTS FOR METALS

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ABSTRACT

Coatings produced from zinc oxide and polyphosphoric acid did not resemble those produced from zinc oxide (ZnO), dimethyl hydrogen phosphite (DMHP), and ethyl acid phosphate (EAP).

Coatings (ZnO-DMHP-EAP) cured above 55% relative humidity at 100°F were water resistant but not heat resistant, while those cured below 55% were heat resistant but not water resistant. At 136°F, the similar critical relative humidity value was earlier found to be 38%.

Water-resistant coatings prepared from ZnO-DMHP-EAP were more insoluble in water than coatings prepared from the same materials that were not water resistant. The zinc in the water-soluble fractions of these coatings was present as ions, or it was present in some form that was easily ionized when dissolved in water.

When the ZnO-DMHP-EAP coating material was dissolved in DMHP and the solution was applied to aluminum, a crusty layer was obtained. When the crust was removed, a surface coating remained that was heat resistant, water resistant, coherent, hard, and firmly bound to the aluminum. Attempts are now being made to duplicate these results.

THE DEVELOPMENT OF HEAT-RESISTANT PAINTS FOR METALS

I. INTRODUCTION

The purpose of this project is to develop protective coatings for metals that can be bonded without heating and that will withstand high temperatures. This type of heat-resistant paint is needed for certain aircraft and space-craft applications in which it is not practical to heat cure the coating to promote bonding. Yet the coating must protect the metal substrate at the high temperature that may be developed in flight at high speeds as well as against corrosion and erosion under normal atmospheric conditions.

The present contract provides for continuation of the work carried out for the Bureau of Weapons under previous contracts NO-as-60-6075-c and NOW-6f-0546d.

In the earlier studies, combinations of a large number of metal oxides and ceramic frits with various liquid organophosphorus compounds were investigated for making coatings with the desired characteristics. The results of these studies showed that well-bonded, heat-resistant coatings that could be cured at low temperatures could be made from metal oxides and phosphorus compounds. For example, coatings were made by application of a mixture of zinc oxide, dimethyl hydrogen phosphite (DMHP), and ethyl acid phosphate (EAP) to aluminum that were well bonded to the substrate and that were resistant to wet abrasion, to heating at 1000°F for over 200 hours, and to thermal shock due to heating to 1000°F and quenching in cold water. However, coatings with these properties could not be produced consistently. Studies of reaction mechanisms and of the effects on coating properties of additives and of variations in methods of preparing and applying the coating mixtures, in curing conditions, and in the components and component ratios were not complete at the time of expiration of the previous contract.

In resuming these studies under the current contract, efforts have been made to learn more about the chemical nature of the coating formed by the metal oxide-organophosphorus compound reaction system and the reactions by which it is formed. The basic coating mixture used for most of the current work has consisted of 10 parts of zinc oxide, 12 parts of DMHP and 1 part of EAP. To explore the possibility of a polyphosphoric acid being an intermediate in the metal oxide-organophosphorus

compound reaction system, preliminary experiments have been conducted on the reaction of zinc oxide and polyphosphoric acid. Successful preparation of coatings by this reaction would also indicate the possibility of a phosphorus-oxygen-phosphorus linkage comprising the basic macromolecular structure. Experiments were run on coatings that were water resistant and some that were not water resistant in attempts to find indications of the nature of the bonding of the zinc atom in the ZnO-DMHP-EAP coating system.

The studies of the effects of curing temperature, relative humidity, and curing time on the heat resistance and water resistance of ZnO-DMHP-EAP coatings were resumed. The effect of purity of DMHP on coating properties was also investigated.

An approach to the preparation of coatings that was discussed, but not thoroughly investigated during the previous contract period, was to dissolve the coating material formed by the reaction of zinc oxide and organophosphorus compounds to prepare a solution of the heat-stable reaction product that could be applied easily to a metal surface. If this could be accomplished, less concern over conditions of application might be necessary. For example, curing conditions and reaction time would not be as critical at the time the coating was applied. During this report period, studies of the use of DMHP as a solvent for the ZnO-DMHP-EAP reaction product were initiated.

II. SUMMARY

1. Reactions of zinc oxide and polyphosphoric acid, which was prepared by reacting orthophosphoric acid and phosphorus pentoxide, yielded crusty, hard products with no cohesive strength or film integrity. Although the evaluation of these products has not been completed, these products did not resemble the coatings prepared from ZnO-DMHP-EAP.

2. Addition of sodium ferrocyanide to the water extracts of ZnO-DMHP-EAP coatings precipitated zinc ferrocyanide. The result indicated the zinc in the water-soluble fractions of the ZnO-DMHP-EAP coatings was present as ions, or it was present in some form that was easily ionized when dissolved in water. There was less of this water-soluble zinc in the water-resistant coating than in the coating that was not water resistant.

The zinc present in the water-insoluble fraction of the water-resistant coating was not readily accessible for exchange with calcium, when the water-insoluble fraction was digested in a 10% aqueous solution of calcium chloride.

3. At a curing temperature of 100°F, coatings cured above 55% relative humidity were water resistant but not heat resistant, while those cured below 55% were heat resistant but not water resistant. In earlier studies, the critical relative humidity at a curing temperature of 136°F was found to be 38%. Studies are now being conducted at 72°F and different relative humidities.

4. Increasing the curing time from 2 to 24 hours had no effect on the water and heat resistance of the ZnO-DMHP-EAP coating cured at 100°F at 20 or 50% relative humidity.

5. Coatings prepared with commercial DMHP and coatings prepared with the DMHP by distillation had similar properties.

6. A solution of the ZnO-DMHP-EAP coating material in DMHP was applied to aluminum panels and allowed to stand for 24 hours. Subsequent heating of the panel to drive off volatiles resulted in an easily removed crust being formed on the panel. After the crust was removed, a surface coating remained on the aluminum that was coherent, heat resistant, water resistant, and fairly hard. The solution and the coating will be studied further.

III. MATERIALS AND PROCEDURES

A. Materials

The organophosphorus compounds used during this report period were commercial-grade products that were obtained from the Virginia Carolina Chemical Corporation. The other chemicals used were reagent-grade products that were obtained from General Chemical Division of Allied Chemical Corporation. The aluminum for the coating substrate was Alclad 2024-T3. These are the same grades of materials that have been used in the previous studies.

B. Coating Evaluation Procedures

After application to the aluminum substrate and curing, the coatings were evaluated for appearance, hardness, bonding, water resistance, and heat resistance. Hardness was determined by scratching a coating with a fingernail. Bonding was evaluated by bending a coated panel over a conical mandrel (maximum diameter of bend -0.5 in.), and observing the loss of adhesion of a coating at the bend. Water resistance was determined by rubbing a wet coating with a wet paper towel and observing any loss of adhesion to the panel. Heat resistance was determined by placing a coated panel (coated side up) on a laboratory hot plate at 1000°F for 5 minutes, and then quenching it in cold water and observing the effect on the coating.

A rating system similar to the one outlined in the final report on Contract NO-as-60-6075-c (February 3, 1961) was used to indicate the performance of coatings. In this system, numbers from 1 to 4 are used to indicate the performance of coatings as follows:

Hardness

Rating 1 • very hard, cannot be scratched by a fingernail

Rating 2 • hard, can be scratched by a fingernail if moderate pressure is applied

Rating 3 • soft, can be easily scratched by a fingernail

Rating 4 - very soft, can be rubbed off panel with finger

Surface appearance of coating after curing at room temperature

Rating 1 • smooth, even surface

Rating 2 • rough, uneven surface

Bonding

Rating 1 - good bonding, no loss of coating on bending panel over a 0.5-in.-diameter mandrel

Rating 2 - fair bonding, very slight damage at unprotected edges of panel on bending over a 0.5-in. diameter mandrel

Rating 3 - poor bonding, considerable loss of coating on bending panel over a 0.5-in. diameter mandrel

Water resistance (wet abrasion method)

Rating 1 - insoluble and tightly adhered to panel

Rating 2 - insoluble but only partially adhered to panel

Rating 3 - soluble, not adhered to panel

Heat resistance - 1000°F for 5 minutes plus quenching

Rating 1 - not damaged

Rating 2 - very slightly damaged at unprotected edges

Rating 3 - badly damaged, coating flaked off or foamed

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Studies of the Structure of the ZnO-DMHP-EAP Coating

1. Reaction of zinc oxide with polyphosphoric acid

The reaction of ZnO with polyphosphoric acid is being studied with the expectation that knowledge of this reaction and the products formed will shed some light on the nature of the reaction occurring in the zinc oxide-dimethyl hydrogen phosphite (DMHP)-ethyl acid phosphate (EAP) mixtures and on the structure of the products of this reaction.

Polyphosphoric acid was prepared by the reaction of equimolar quantities of orthophosphoric acid and phosphorus pentoxide under nitrogen at 225-250°C for 10 hours.¹ The reaction product was a light yellow syrup which was difficultly soluble in water.

Four blends containing 10 parts of polyphosphoric acid and 1, 2, 5, or 10 parts of ZnO were prepared, and attempts were made to form coatings of them on aluminum panels. The reaction products formed hard, brittle, discrete agglomerates; none of them formed a coherent coating on the aluminum. The products will be studied to determine their characteristics and further attempts will be made to prepare coatings of this type.

2. Nature of bonding of zinc in ZnO-DMHP-EAP coating

Studies have been initiated to determine the nature of the bonding of the zinc in ZnO-DMHP-EAP coatings that are not water resistant and in those coatings that are water resistant.

Samples of both types of coatings were prepared by casting the basic ZnO-DMHP-EAP formulation on glass plates and by curing it at 100°F under the proper humidity conditions. The coatings were scraped from the plates, weighed, and suspended separately in water heated to 60°C for several hours. The mixtures were then filtered.

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1. E. L. Geftter, "Organophosphorus Monomers and Polymers," Associated Technical Services, Inc., Glen Ridge, New Jersey, 1962, p 240.

and the residues were washed several times with distilled water, dried, and weighed.

Both the water-resistant and the nonwater-resistant coatings were found to be partially soluble in water. The coatings that were not water resistant were more soluble than the coatings that were water resistant. About 41% of the coating that was not water resistant was soluble, and about 17% of the coating that was water resistant was soluble.

Sodium ferrocyanide was added to the filtrates and zinc ferrocyanide precipitated. Approximately 2.7 times more precipitate was obtained from the filtrate of the coating that was not water resistant than from the filtrate of the water-resistant coating. This difference in the amounts of zinc ferrocyanide precipitate from the two types of coatings agrees with the difference in the solubilities of the coatings, as would be expected. These results indicate that the zinc present in the water-soluble fractions of the coatings was present as ions or in some form that was easily ionized when dissolved in water.

The insoluble residue from the water-resistant coating was suspended in a 10% aqueous calcium chloride solution, and the suspension was heated at near boiling for several hours, while being stirred, and then it was allowed to stand for 7 days. The suspension was filtered, and the residue was washed several times with distilled water and then dried. Spectrographic analysis of the residue showed that it contained only 0.1% calcium. If the zinc present in the insoluble residue of the water-resistant coating was present as easily replaceable ions, we would have expected the coating to have contained more calcium.

B. Effects of Reaction Variables on the Properties of the ZnO•DMHP-EAP Coating System

1. Curing temperature, relative humidity, and time

Experiments have been conducted to study the effects of curing temperature and relative humidity on coating properties. During the previous contract period, experiments were conducted at curing conditions of 136°F and relative humidities ranging from 20 to 70%. Experiments at 300°F and relative humidities ranging from 20 to 60% were made during this report period, and experiments at 72°F and different relative humidities are now under way.

Coatings evaluated were basically 10 parts of ZnO, 12 parts of DMHP, and 1 part of EAP. Varying amounts of distilled water were added to some of the blends. The blending procedure was as follows: The ZnO was added to the DMHP and the mixture was stirred for 75 seconds and then the EAP and water were added and the mixture stirred for an additional 15 seconds. The mixing was done in a Waring Blendor or in a beaker with a spatula. Coatings were doctored onto aluminum panels that had been sanded lightly, rinsed with acetone, and air-dried. As in our previous study, the coated aluminum panels were placed in a controlled environment within 10 minutes after application of the coating to the panel.

As shown by the data in Table I, the coatings cured at 100°F and a relative humidity above 55% were water resistant; the coatings cured at 100°F and a relative humidity below 55% were not water resistant. Conversely, the coatings cured at relative humidities above 55% were not heat resistant and those cured at relative humidities below 55% were heat resistant. At 136°F, the similar critical relative humidity value was earlier found to be 38%. A curing temperature of 72°F and different relative humidities are now being studied and initial results indicate that there is also a critical relative humidity value at this curing temperature. Reasons for the properties of the coatings to depend upon the humidity during curing are being sought, and then attempts will be made to prepare coatings with properties less sensitive to the relative humidity during curing.

The heat resistance and water resistance of coatings cured at 100°F and 20 or 50% relative humidity for 2 hours and for 24 hours are given in Table II. All of the coatings had the same resistance to heat and water.

2. Purity of DMHP

It was thought that impurities present in commercially supplied DMHP might be the cause of some of the inconsistencies in properties obtained with the ZnO-DMHP-EAP coatings. Coatings prepared from the following formulations were evaluated to compare distilled and undistilled DMHP:

- (1) 10 parts of ZnO, 12 parts of DMHP
- (2) 10 parts of ZnO, 12 parts of DMHP, 1 part EAP
- (3) 10 parts of ZnO, 12 parts of DMHP, 1 part water

Table I. Effects of Curing Conditions on Water and Heat Resistance of Coatings

Coating composition, parts by weight ^a				Curing conditions		Ratings of coatings cured 1 day	
ZnO	DMHP	EAP	Water	Relative humidity, %	Temperature, °F	Water resistance	Heat resistance
10	12	1	-	20, 28, 50	100	3	1
10	12	1	1	20, 28, 50	100	3	1
10	12	-		55	100	3	1
10	12	1		55	100	3	3
10	12	1	-	57	100	1	2
10	12	1	1	57	100	1	3
10	12	1	4	57	100	1	2
10	12	1	-	60	72	3	1
10	12	1	1	60	72	3	1
10	12	1	4	60	72	3	1

^aDMHP = dimethyl hydrogen phosphite; EAP = ethyl acid phosphate.

Table II. Effect of Curing Time on Heat Resistance and Water Resistance
of Coatings Cured at 100°F and Different Relative Humidities

Coating composition, parts by weight ^a				Curing conditions			Ratings of coatings cured 1 day	
ZnO	DMHP	EAP	Water	Relative humidity, %	Temperature, °F	Time, hr	Water resistance	Heat resistance
10	12	1	-	50	100	2	3	1
10	12	1	-	50	100	24	3	1
10	12	1	1	50	100	2	3	1
10	12	1	1	50	100	24	3	1
10	12	1	-	20	100	2	3	1
10	12	1	-	20	100	24	3	1
10	12	1	4	20	100	2	3	1
10	12	1	4	20	100	24	3	1

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^aDMHP = dimethyl hydrogen phosphite; EAP = ethyl acid phosphate.

The DMHP was fractionally distilled under a nitrogen atmosphere at 17 mm pressure, and the fraction boiling between 68.5°C and 70°C was collected, and used. This fraction represented 95% of the original charge.

The coatings prepared with the distilled DMHP did not differ in heat resistance or water resistance from the coatings prepared with undistilled DMHP.

C. Evaluation of DMHP as a Solvent for the ZnO-DMHP-EAP Coating

It had been postulated earlier that the coatings prepared from ZnO, DMHP, and EAP consisted of a polymeric material, which served as a binder, and of unreacted ZnO. If the coating material could be dissolved in a solvent and applied to metals, the conditions for curing the coating may be of less concern. Previous attempts to find a solvent for the coatings were unsuccessful, but during this report period, it was found that coatings heated to 1000°F for 5 minutes could be dissolved in an excess of DMHP. The heated coatings were water resistant.

A number of panels that had been coated with a ZnO-DMHP-EAP formulation were immersed in DMHP overnight. The coatings completely dissolved. Approximately 75% of the DMHP was distilled from the solution under reduced pressure, and the residue was applied to aluminum panels. After 24 hours at room temperature, the coating was not dry, presumably because of the low volatility of the DMHP. However, when the panels were heated on a hot plate to 1000°F, the volatile portion of the coatings was removed, and a crusty, brittle solid remained on the panels. This solid material came loose from the panel when the panel was placed in water, leaving a thin coating on the surface of the panel that was heat resistant, hard, water resistant, and well bonded to the aluminum. It has not been determined whether a separate coating was deposited on the surface of the aluminum panel or whether the surface of the panel was converted to a complex aluminum-phosphorus-oxygen salt. Investigations of the coating are being continued.

V. FUTURE WORK

The study of the chemical nature of the ZnO-DMHP-EAP coatings will be continued. Elemental analyses will be obtained on the soluble and insoluble portions of coatings that are water resistant and coatings that are not water resistant. Attempts will be made to determine how the zinc is bound in the insoluble portion of both types of coatings. The water content of coatings and the amount of volatile products produced when the coatings are cured under different conditions of temperature and relative humidity will be determined.

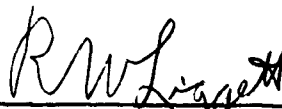
The study of the treatment of aluminum with dissolved ZnO-DMHP-EAP coatings will be continued.

The thermal stability and water solubility of the agglomerates formed by the reaction of polyphosphoric acid and zinc oxide will be determined, and additional techniques for obtaining coatings through the polyphosphoric acid-zinc oxide reaction will be tried. If possible, polyphosphate esters will be prepared and reacted with zinc oxide.

VI. ACKNOWLEDGMENTS

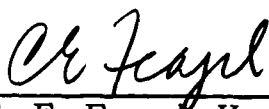
Experimental work on the project was performed by Mr. Marvin McGarity, Assistant Chemist, Mr. Franklin Alexander, Technical Assistant, and Mr. Stanley E. Mileski, Associate Chemist. Mr. Mileski has also assisted in writing this report.

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